The Properties of a New Transparent and Colorless Barrier Film

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Keywords: Al_2O_3 films; SiO_2 films; E-beam evaporation; Permeation barrier coatings

Abstract

A new ceramic-coated PET barrier film has been developed. This paper describes the properties of this new ceramic-coated barrier film. The following performances appear at a ceramic-layer thickness greater than 180Å.

- **high barrier**
  - **OTR<1.0cc/m²·day**
  - **WVTR<1.5g/m²·day**
- **good flexibility**
- **colorless transparency**

This new ceramic thin film is deposited by the EB-evaporation method using EB gun. It is a high production method similar to Al metal coating, but this ceramic layer needs a thickness of only 180Å. We anticipate low cost barrier film from this development.

Introduction

Considerable development efforts on transparent ceramic-coated barrier film have taken place, but few manufacturers have released SiO_x- and Al_2O_3-coated films to the market. In spite of such efforts, no remarkable market growth in this packaging field has yet occurred.

Reviewing the existing state of coating materials, four main technologies have been reported, and we are able to classify 4 typical types of barrier films in table 1. SiO_x (x=1.5~1.8) is the most popular and has been the subject of long-term research. Consequently, SiO_x-coated barrier film entered practical applications early. But raw material costs are overly expensive, and SiO_x-coated film is yellowish. Thus this type has not shown strong growth.

The second type is colorless transparent SiO_2 deposited by the plasma-enhanced chemical vapor deposition method. In recent years, several types of modified CVD methods have been reported [1][2], and offer good performance.

Table 1 Summary of Ceramic Barrier Coatings on PET.

	1	2	3	4
Material	SiO_x (x=1.5~1.8)	SiO_2	Al_2O_3	Double layer SiO_2/Al_2O_3 SiO_2/SiO
Deposition Methods	Evaporation	PE-CVD	Reactive Evaporation	Evaporation
Thickness(Å)	400 ~800	150	250	500/25
OTR (cc/m²·day)	1~2	1	2~4	2~3
Color	Yellow	Clear	Clear	Clear

Table 2 Pre-Examination Summary of SiO_2 Thin Films

Deposition Method	PE-CVD	Sputtering	EB-Evaporation
OTR (cc/m²·day)	4	0.5	15~70
Deposition Rate (Å/sec.)	5	1	2000
Thin Film Density (g/cc)	2.1	2.1	1.95

38th Annual Technical Conference Proceedings (1995) ISSN 0737-5921

The third type is typically referred to as Al_2O_3 deposition by the reactive evaporation method. This method can achieve high deposition rates nearly equal to Al metal deposition. One disadvantage of this material is its easy fragility in comparison with SiO_x. Recently, strong and thin film has been reported by using plasma-enhanced evaporation[3].

The last type is the newest. In recent years several manufacturers have reported constitutions of double ceramic layers. For example [4][5], the first layer of deposited Al_2O_3 acts to smooth the polymer surface and stimulates the growth of a second layer of SiO_2.

We have developed a new ceramics composition and a new evaporation process using an electron beam gun to satisfy packaging film requirements. Such packaging film requirements mean high barrier performance, good flexibility, colorless transparency and low cost. This report presents some experimental results concerning this new transparent barrier film.

Pre-examination

In our approach, we analyzed thin SiO_2 coatings on PET film deposited by PE-CVD, sputtering and evaporation methods in batch-type apparatus.

According to Table 2, in the case of the evaporation method barrier performance was lacking, confirming this well-known fact. It must be noted that with PE-CVD and sputtering, thin film density has a high value. But with the evaporation method density is low. Accordingly, the thin film structure deposited by evaporation is porous, raising the next concerns. In this film, numerous incomplete bonds exist between Si and O atoms, thus we have to bond Si and O using other atoms or by using another deposition process. When achieved, barrier performance improved as relative material density increased.

Experimental

According to the situation described above, we tried to add various kinds of metals and metal oxides to SiO_2 to reduce the number of incomplete bonds between Si and O.

Some of the various SiO_2 mixtures dissolved in boiling water and others lacked barrier performance. Ultimately, using SiO_2 mixed with Al_2O_3, we were able to develop a new clear transparent barrier film having high performance and good applicability.

Results

1. Sample making apparatus

EB-evaporation apparatus is shown in Fig. 1.

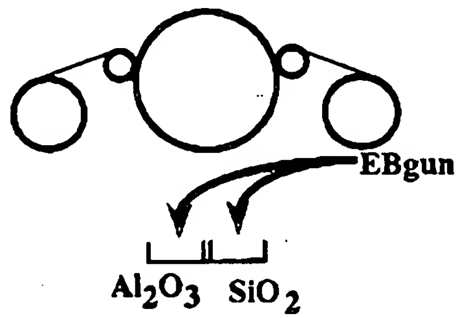

Fig. 1 Schematic of research EB evaporation apparatus

Al_2O_3 and SiO_2 are simultaneously vaporized by EB-gun. Al_2O_3 and SiO_2 vapor mix at the surface of the web film, and this vapor mixture is introduced to form the coating layer.

2. Evaluation

2.1 Relative density and oxygen permeability

For coating confirmation, evaluation of relative density dependence on adding Al_2O_3 to SiO_2 is very important. Fig. 2 shows the Al_2O_3 proportion increase and the increase in the relative density of mixed thin film: with Al_2O_3 at 30%, relative density exceeds 95%. This value is equal to that of PE-CVD and sputtering. In contrast, OTR and WVTR improve the proportion of Al_2O_3 content. Above 35%, OTR is less than 2cc/m²·day. This thin film has clear transparency of course (Fig. 4).

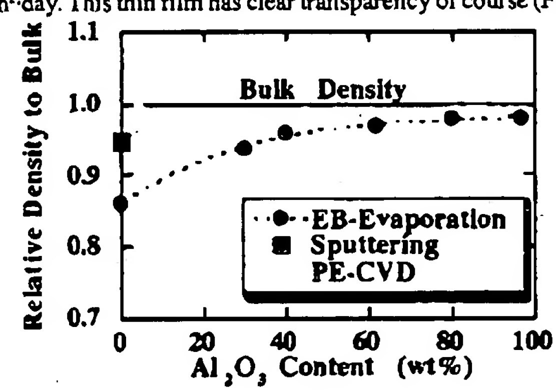

Fig. 2 Thin film relative density to bulk versus Al_2O_3 contents in new ceramic layer.

2.2 Evaluation of laminated film

Ordinarily, ceramic-coated barrier films are used after lamination. To optimize laminating conditions, barrier film elongation and gravure pressure were investigated.

OTR dependence on stretching treatment is shown in Fig. 5[6]. The new materials and SiO_2 exceed Al metal in substrate elongation. Al_2O_3- and SiO_x- coated film is quite fragile in comparison with SiO_2 and developed material.

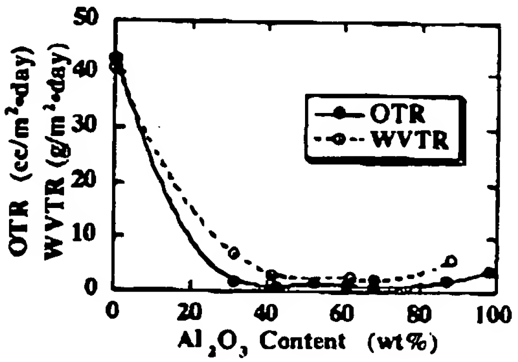

Fig. 3 Oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) versus Al_2O_3 content in new ceramic layer.

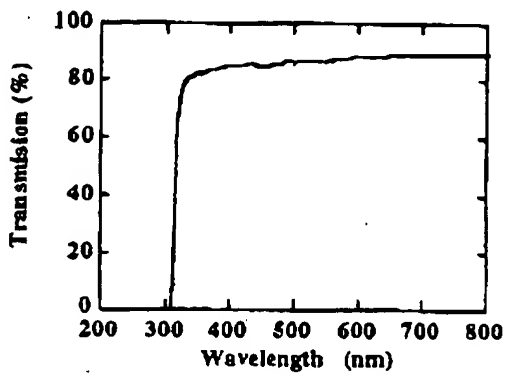

Fig. 4 Transparency of new ceramic-coated $12\mu m$ PET versus light wavelength.

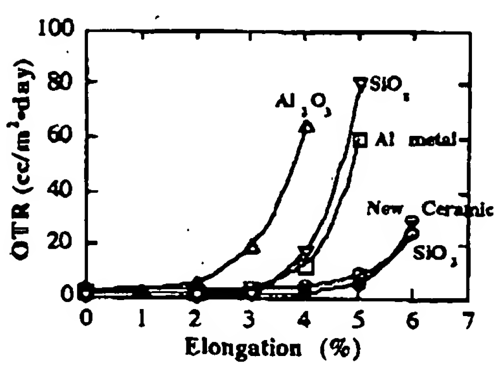

Fig. 5 Oxygen transmission rate (OTR) versus elongation of new ceramic, SiO_2, SiO_x, Al_2O_3, Al metal-coated $12\mu m$ PET.

OTR dependence on gravure pressure is important for estimating suitability for lamination and printing processing. Fig. 6 shows the relationship between OTR and gravure pressure. On the basis of this curve, the new ceramic film will withstand $20kg/cm^2$. Similarly to film elongation, Al_2O_3- and SiO_x-coated films crack more easily than Al metal, SiO_2 and developed materials.

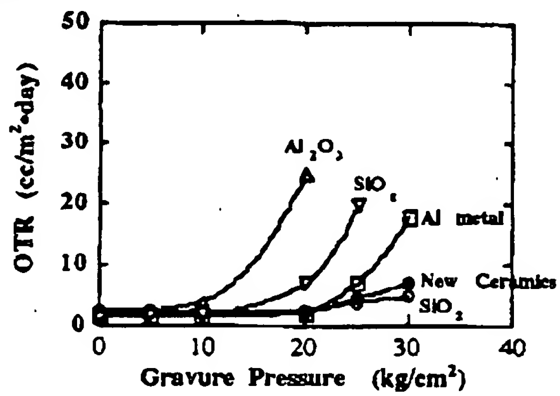

Fig. 6 Oxygen transmission rate (OTR) versus gravure pressure of new ceramic, SiO_2, SiO_x, Al_2O_3, Al metal-coated $12\mu m$ PET.

The properties elongation and gravure pressure of the new ceramic material are sufficient for achieving practical lamination processing.

As one practical test, Table 3 shows the test results after lamination with CPP($60\mu m$). OTR is established over a range f coating thicknesses exceeding 180Å (Fig. 7). To observe post-lamination characteristics, we used 200Å-coated PET. Lamination conditions follow:

substrate: PET $12\mu m$
ceramic thickness: 200Å
laminated film: CPP $60\mu m$
adhesion: polyurethane
film tension: 50kg/m (elongation: <3%)
pressure : adhesion coat $10kg/cm^2$
: lamination:$3k\ g/cm^2$

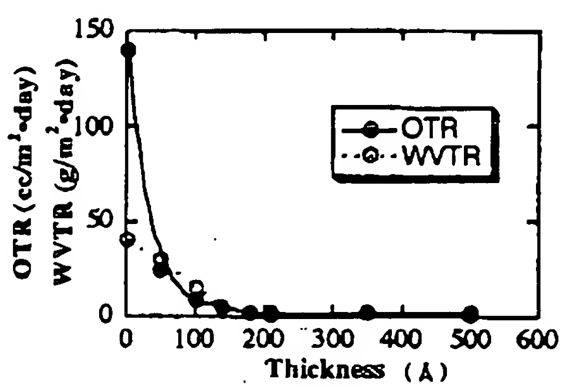

Fig. 7 Oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) versus thickness of coating layer.

Table 3 Results of New Ceramic Barrier C ating after Lamination with CPP 60μm.

	OTR ($cc/m^2 \cdot day$)	WVTR ($g/m^2 \cdot day$)
Lamination	1.0	1.0
Lamination Boiling Water 90°C-30min.	1.3	1.7
Lamination Gelbo test 50 times	3.1	1.3

2.2.1 OTR and WVTR

Adhesive lamination reduces OTR by 0~200% compared to unlaminated film. WVTR improves also. The reason for this has not yet been identified, but OTR reaches <1.0cc/m^2·day and WVTR <1.5g/m^2·day. OTR and WVTR are equivalent to SiO_2 by PE-CVD after dipping into boiling water. In addition, test barrier performance after gelbo is equivalent to SiO_2.

2.3 Coating speed

Web speed coating of the new ceramic can achieve 230m/minutes. However, mechanical limitations of web equipment determine web speed.

Also, thin film composition is homogeneous in the depth direction using electron spectroscopy for chemical analysis (ESCA) when web speed is 230m/min.

3 Conclusions

A new ceramic which is composed of SiO_2 and Al_2O_3 mixture coated on 12μm PET film is discussed in this paper. The following conclusions have been reached: (1) It is possible for this new ceramic-coated 12μm PET film to achieve an OTR of less than 1.0cc/m^2·day and a WVTR of less than 1.5g/m^2·day. (2) The new ceramic-coated 12μm PET film has high flexibility. (3) This barrier film offers colorless transparency. (4) The new ceramic thin film can be deposited by EB-evaporation at a web speed of more than 230m/min. We anticipate low cost barrier film as a result of this development.

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